

## EMULSIFIER

10 Valerie Bonnardel  
Florence Catterson  
Anja Gestmann

### SUMMARY OF THE INVENTION

15 The present invention relates to a novel emulsifier which comprises at least one pregelatinized, crosslinked starch selected from a C<sub>2</sub>-C<sub>5</sub> hydroxyalkyl starch and a C<sub>2</sub>-C<sub>18</sub> acyl starch and at least one starch derivative containing a hydrophobic group or both a hydrophilic group and a hydrophobic group, which has been degraded by reaction with an exo-enzyme capable of cleaving 1,4- $\alpha$ -D-glucosidic linkages from non-reducing ends of starch, but incapable of cleaving  
20 1,6- $\alpha$ -D-glucosidic linkages of starch. Such emulsifier achieves stable compositions, which are salt tolerant and do not exhibit tackiness. Further, the emulsifier is ethoxylate-free and may be used in a variety of compositions, including cosmetic compositions.

### 25 DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a novel emulsifier. The emulsifier comprises two components prepared from base starches. Base starch, as used herein, is intended to include all starches derived from any native source, any of which may be suitable for use herein. A native starch, as used herein, is one as it  
30 is found in nature. Also suitable are starches derived from a plant obtained by standard breeding techniques including crossbreeding, translocation, inversion, transformation or any other method of gene or chromosome engineering to include variations thereof. In addition, starch derived from a plant grown from artificial mutations and variations of the above generic starch, which may be  
35 produced by known standard methods of mutation breeding, are also suitable herein.

Typical sources for the starches are cereals, tubers, roots, legumes and fruits. The native source can be waxy varieties of corn (maize), pea, potato, sweet potato, banana, barley, wheat, rice, oat, sago, amaranth, tapioca

5 (cassava), arrowroot, canna, and sorghum, as well as low and high amylose varieties thereof. As used herein, the term "low amylose" starch is intended to include a starch containing no more than about 10%, particularly no more than 5%, more particularly no more than 2% amylose by weight. As used herein, the term "high amylose" starch is intended to include a starch containing at least  
10 about 50%, more particularly at least about 70%, more particularly at least about 80% amylose by weight.

The first component comprises at least one pregelatinized, crosslinked starch selected from a C<sub>2</sub>-C<sub>5</sub> hydroxyalkyl starch and a C<sub>2</sub>-C<sub>18</sub> acyl starch.

The first component is pregelatinized. Pregelatinization and techniques  
15 for achieving pregelatinization are known in the art and disclosed for example in U.S. Patent Nos. 4,465,702, 5,037,929, 5,131,953, and 5,149,799. Also see, Chapter XXII- "Production and Use of Pregelatinized Starch", Starch: Chemistry and Technology, Vol. III- Industrial Aspects, R.L. Whistler and E.F. Paschall, Editors, Academic Press, New York 1967. The term pregelatinized is intended to mean swollen starch particles, which have lost their birefringence and/or Maltese crosses in polarized light. Such pregelatinized starches derivatives are substantially soluble in cold water without cooking. In this context "soluble" does not necessarily mean the formation of a true molecular solution, but may also mean a colloidal dispersion. In one embodiment, the starch is completely  
20 pregelatinized.  
25

Pregelatinization may be achieved by methods which include, without limitation, drum drying, extrusion and spray drying. In one embodiment, extrusion is used for the simultaneous cooking and drying of the starch (see for example US 3,137,592). This process makes use of the physical processing of a  
30 starch/water mixture at elevated temperatures and pressures which brings about the gelatinization of the starch, followed by expansion after leaving the nozzle with sudden evaporation of the water.

In one embodiment, pregelatinization is complete to provide good solubility and eliminate undissolved particles, which may give rise to an  
35 unpleasant, sandy feel in the composition.

In one embodiment, the starch has a majority of intact starch granules. Aqueous dispersions of pregelatinized starch derivatives having a largely intact granular structure typically have a more uniform smooth texture than aqueous

5 dispersions of starches without a granular structure, which may have a slightly gritty feel. In the case of pregelatinized starches with an intact granular structure, the native internal structure of the hydrogen bonds is destroyed, but the external shape or form is maintained.

Another embodiment of this invention uses the process described in US  
10 4,280,851 to produce the pregelatinized starch. An apparatus adapted for carrying out the process is described in US 4,600,472. In this process a mixture of the granular starch or starch derivative is cooked or gelatinized in the atomized state. The starch to be cooked is atomized through an atomizing opening into a nozzle arrangement in order to form a relatively finely divided sprayed material.  
15 In addition, a heating medium is injected through an opening in the nozzle arrangement into the sprayed material so as to heat the starch to the temperature necessary for gelatinization. A closed chamber surrounds the injection openings for the atomizing and heating medium and defines a ventilation opening positioned in such a way that the heated starch spray material can leave the  
20 chamber. The arrangement is such that during the passage of the starch spray material through the chamber, that is from the atomizing opening to the ventilation opening, the time elapsed defines the starch's gelatinization time. The resulting spray dried, pregelatinized starch includes uniformly gelatinized starch granules, and the granules are in the form of indented spheres, and are mostly  
25 whole and unbroken and swollen after hydration. Nozzles usable for producing such starches are also described in US 4,610,760.

For the production of suitable pregelatinized starches it is also possible to use the process of US 5,149,799. In this process starch is uniformly atomized and cooked by means of a single atomization stage in the presence of an  
30 aqueous medium. The atomization stage is performed in an apparatus having an internal mix, two-fluid spray drying nozzle, and it is coupled to a device for drying the cooked, atomized starch.

Spray dried, pregelatinized starches with suitable characteristics can also be produced by a continuous, coupled jet-cooking and spray-drying process. In  
35 one embodiment of this process, a starch suspension is gelatinized at 138 to 160°C in a jet cooker with direct steam injection. The streams of starch suspension and steam are mixed in a cooking or boiling chamber. The outlet of the latter is connected to a pneumatic spray nozzle or a high pressure nozzle,

5 which is located in a conventional spray dryer. The jet-cooked starch is directed at elevated temperature and pressure into the spray nozzle and can be atomized with cold air, hot air or steam. After atomizing, the hot, jet-cooked starch solution is handled in the same way as conventional spray dried starches. The drying process is adequately fast to prevent retrogradation of the starch molecules  
10 during the cooling and drying of the droplets. The spray dried starch is an amorphous material (i.e., it is substantially non-crystalline) that is easily soluble in water or colloiddally dispersible.

The dried product may further be agglomerated.

The first component is also crosslinked. Crosslinking of the starch  
15 chains can be achieved by suitable crosslinking agents, that is bifunctional compounds. In one embodiment, the crosslinking method used is phosphorylation, in which the starch is reacted with phosphorous oxychloride, phosphorous pentoxide, and/or sodium trimetaphosphate. Two starch chains are crosslinked by an anionic P-O group. The anionic character of the crosslinking  
20 sites assists the emulsion-stabilizing action of the starch to be used according to the invention. In another embodiment, the crosslinking method is by means of C<sub>4</sub>-C<sub>18</sub> alkane or alkene dicarboxylic acids which include without limitation C<sub>4</sub>-C<sub>8</sub> alkane dicarboxylic acids, exemplified by adipic acid. The alkane or alkene dicarboxylic acid links two starch chains via ester bonds. It can be in straight or  
25 branched chain form. The derivatives may be obtained, for example, by reacting starch with the mixed anhydrides of dicarboxylic acid and acetic acid. In one embodiment, less than 0.1 weight percent based on the dry starch crosslinking agent is used. In another embodiment, about 0.06 to 0.1 weight percent based on the dry starch crosslinking agent is used.

30 The first component is further modified to either a C<sub>3</sub>-C<sub>5</sub> hydroxyalkyl starch or a C<sub>2</sub>-C<sub>18</sub> acyl starch. Such modifications and the techniques to achieve them are well known in the art.

In one embodiment, the starch is a C<sub>3</sub>-C<sub>5</sub> hydroxyalkyl starch. The position of the hydroxyl group, which is bound to the starch backbone via an alkyl  
35 group with 3 to 5 carbon atoms in the alkyl group, is not critical and can be in the alpha to omega position. In one suitable embodiment, the degree of substitution of the hydroxyalkylation is about 0.08 to 0.3. The degree of substitution is the average number of substituted OH groups of the starch molecule per

5 anhydroglucose unit. The hydroxyalkylation of a starch can be brought about by reacting a native starch with alkylene oxides with the appropriate number of carbon atoms, including without limitation hydroxypropylation by reaction of the starch with propylene oxide. A starch to be used according to the invention can also contain more than one hydroxyl group per alkyl group.

10 In another embodiment, the starch is a C<sub>2</sub>-C<sub>18</sub> acyl starch. This starch may be achieved if the crosslinking has been brought about by C<sub>4</sub>-C<sub>18</sub> alkanooate or alkenoate and may be additionally acylated with a view to a suitable hydrophilic-lipophilic balance with a degree of substitution in one embodiment of 0 to 0.8 and in another of 0 to 0.5. Acylation may be achieved by reaction with acid  
15 anhydrides of the general formula (R-C(O))<sub>2</sub>O, in which R is an alkyl group, such as methyl or ethyl, with succinic or maleic anhydride or their alkylated derivatives.

Suitable embodiments for the first component include without limitation hydroxypropyl di-starch phosphate and acetylated di-starch adipate. Also suitable are such starches derived from low amylose corn starch.

20 The processes use to prepare the first component may be conducted in any order. However, one skilled in the art would understand the advantages of certain orders. For example, hydroxypropylation would typically be conducted before crosslinking with phosphorous oxychloride as the typical hydroxypropylation process would destroy some of the crosslinking achieved.

25 The second component comprises at least one starch derivative containing a hydrophobic group or both a hydrophilic group and a hydrophic group, which has been degraded by reaction with an exo-enzyme capable of cleaving 1,4- $\alpha$ -D-glucosidic linkages from non-reducing ends of starch, but incapable of cleaving 1,6- $\alpha$ -D-glucosidic linkages of starch.

30 In one embodiment, the starch of the second component will be a pregelatinized starch derivative. Pregelatinization is achieved by the methods known in the art as described, *supra*.

The starch of the second component may also be converted, including without limitation fluidity or thin-boiling starches prepared by oxidation, enzyme  
35 conversion including without limitation by  $\alpha$ -amylase, mild acid hydrolysis, heat dextrinization, or mannox (manganese catalyzed degradation of starch as taught for example in US 4,838,944). Such methods are well known in the art. (See e.g., M. W. Rutenberg, "Starch and Its Modifications" in Handbook of Water-

5 Soluble Gums and Resins, R. L. Davidson, editor, McGraw Hill, Inc., New York, N.Y., 1980, pp. 22-36) and/or US 4,035,235. A combination of one or more of these conversion techniques may be used.

The starch is derivatized by treatment with at least one reagent containing a hydrophobic moiety and may additionally contain a hydrophilic  
10 moiety. The hydrophobic moiety may be an alkyl, alkenyl, aralkyl or aralkenyl group that contains at least five carbon atoms, and in one embodiment five to twenty-four carbon atoms. In one embodiment, the hydrophilic moiety may be contributed by the reagent, or, as in another embodiment, the starch's own hydroxyl groups serve as the hydrophilic moiety and the reagent only contributes  
15 a hydrophobic moiety.

In one embodiment, the starch is derivatized by reaction with an alkenyl cyclic dicarboxylic acid anhydride by the method taught in US 2,661,349. However, any process for derivatizing starch which yields the desired blend of hydrophobic and hydrophilic functions on the starch molecule may be used to  
20 derivatize the starch of the second component.

One suitable derivatization of the present invention is an octenylsuccinate half ester derivative of a low amylose starch which has been converted to a Water Fluidity (WF) of up to about 60. In another embodiment, the converted starch is treated with at least 0.25%, in yet another with at least 3.0% of  
25 octenylsuccinic acid anhydride, and in still another with at least 3.0% of dodecenylsuccinic acid anhydride. In a further embodiment, the converted starch is further modified by hydroxyalkylation, as described *supra*. Water Fluidity is an empirical test of viscosity measured on a scale of 0-90 wherein fluidity is the reciprocal of viscosity. Water Fluidity of starches is typically measured using a  
30 Thomas Rotational Shear-Type Viscometer (manufactured by Arthur H. Thomas Co., Philadelphia, Pa. 19106), standardized at 30°C with a standard oil having a viscosity of 24.73 cps., which oil requires 23.12+/-0.05 sec. for 100 revolutions. Accurate and reproducible measurements of the Water Fluidity are obtained by determining the time which elapses for 100 revolutions at different solids levels  
35 depending on the starch's degree of conversion (as conversion increases, the viscosity decreases).

The starch of the second component is further treated with an exo-enzyme. As used herein, exo-enzyme is intended to mean an enzyme capable of

5     cleaving the 1,4-alpha-D-glucosidic linkages from the non-reducing ends of starch, but incapable of cleaving 1,6-alpha-D-glucosidic linkages of starch. Non-limiting examples of the exo-enzymes include beta-amylase, exo-alpha-1,4-glucosidase, exo-1,4-alpha-D-glucan maltotetrahydrolase, and exo-1,4-alpha-D-glucan maltohexahydrolase.

10           The optimum parameters for enzyme activity will vary depending upon the enzyme used. Thus, the rate of enzyme degradation depends on factors including the type and concentration of enzyme used, the type and concentration of starch used, pH, temperature, the presence or absence of inhibitors and other factors. Depending on the type of enzyme, or its source, various parameters may  
15     require adjustment to achieve the desired digestion rate. In one embodiment, the enzyme digestion reaction is carried out at the highest solids content that is feasible to facilitate subsequent drying of the starch while maintaining optimum reaction rates.

          The process of this invention may use an enzyme in solution, an enzyme  
20     immobilized on a solid support, or any other methods of enzyme conversion known in the art.

          At least one buffer may be used to ensure that the pH will be in the optimum or desired range throughout the degradation. Buffers include, without limitation, acetates, citrates and the salts of other weak acids. Other agents may  
25     also be used to optimize enzyme activity. The reaction may be carried out in any pH and temperature range suitable for the enzyme and base starch being used.

          The enzyme reaction is permitted to continue until the desired level of degradation is reached. The progress of enzyme reaction may be measured by various methods, including for example by measuring the concentration of  
30     reducing sugars, the change in viscosity or the change in molecular weight using techniques well known in the art.

          In one embodiment, starch degradation is allowed to proceed to a degree of from 13 to 55%, by weight. In another embodiment, the degradation is allowed to progress until up to 70%, by weight, of the starch, has been hydrolyzed. In yet  
35     another embodiment, the degradation is allowed to proceed until the degradation essentially ceases.

5           After the desired degree of starch degradation has been reached, the enzyme may be deactivated by heat or other methods known in the art. In the alternative, the enzyme is not deactivated.

          In one embodiment, the second component will be hydrolyzed to achieve a dextrose equivalent (DE) of at least about 2, in another embodiment at least  
10       about 5, in a third embodiment at least about 10. Dextrose equivalence, as used herein, is intended to mean the reducing power of a starch hydrolyzate. Each starch molecule has one reducing end: therefore DE is inversely related to molecular weight. The DE of anhydrous D-glucose is defined as 100 and the DE of unhydrolyzed starch is virtually zero. In the alternative, the DE of the blend of  
15       the two components will be at least about 2, in another embodiment at least about 5 in a third embodiment at least about 10.

          In another alternative, sugars may be added to achieve a DE of at least about 2, in another embodiment at least about 5 in a third embodiment at least about 10. In yet another embodiment, the starch derivative of the second  
20       component is not treated with enzymes to achieve in situ sugar formation and sugars are instead added to achieve the same DE level. Sugars, as used herein, is intended to mean mono- di, and oligo-saccharides of up to about 10 glucose units, particularly those of up to about 3 glucose units, such as glucose, fructose, galactose, maltose, isomaltose, sucrose, lactose, raffinose, stachyose,  
25       fructosylsucrose, and maltooligosaccharides, particularly glucose, fructose, and maltose, as well as maltodextrins with a dextrose equivalent of from about 2 to about 50, particularly from about 5 to about 15. The increased DE may result in several advantages such as achieving and maintaining consistently high load levels, low oil exposure, increased oxidation resistance and increased ease of  
30       processing into the end use composition (e.g., cosmetic).

          The practitioner will recognize that the sequence of steps in the process of this invention may be carried out in any order, though certain orders may present certain advantages.

          The first and/or second components may be filtered through a filter aid  
35       such as granular or fibrous solids capable of forming a highly permeable filter cake in which very fine solids or slimy, deformable flocs may be trapped. Two common commercial filter aids are diatomaceous silica (also called diatomite or diatomaceous earth) and cellulosic fibers.



5           If purification is desired, the first and/or second components may be further purified by methods known in the art such as dialysis, filtration, centrifugation or any other method known in the art.

          The pH of the first and/or second component may be adjusted by methods known in the art, for example, by adding suitable pH-regulators, such as  
10   citric acid, lactic acid, phosphoric acid, hydrochloric acid, sodium hydroxide, potassium hydroxide or triethanol amine. When using starch esters, a strong acid pH-value is typically avoided to prevent hydrolysis of the ester bonds. In one embodiment, the emulsifier has a pH value between about 2.5 and 12, in another between about 4 and 9.

15           The first and/or second components may also be dried or otherwise isolated using techniques known in the art, including without limitation spray-drying, drum-drying and freeze-drying. The components may be dried together or individually. In the alternative, the component(s) may be used in liquid or concentrated form. The emulsifier according to the invention can be provided in  
20   either an aqueous form or as a dry powder that is reconstituted in an aqueous medium upon use. The dried component(s) may further be agglomerated.

          The emulsifier may be prepared by mixing the two components together. The ratio of the first component to the second component may be adjusted to  
25   obtain the attributes desired. For example, if more thickening is desired, then more first component should be added, while if more emulsifying is desired, then more of the second component should be added. In one embodiment, the ratio of first component to second component is at least 1:1 and no more than about 4:1 by weight. In another embodiment, the ratio of first component to second component is at least 1:1 and no more than about 3:1 by weight.

30           In one embodiment, the emulsifier comprises a pregelatinized, hydroxypropylated waxy maize starch phosphate and an enzyme converted, octenylsuccinic acid anhydride treated waxy maize starch. In another embodiment, these starches are present in a ratio of 2:1.

          The emulsifier may be used at any level necessary to achieve the  
35   composition characteristics desired. In one embodiment, the emulsifier is used at a level of from about 1 to 10% by weight of the composition. In another embodiment, the emulsifier is used at a level of from about 1 to 7% by weight of the composition.

5           The resultant emulsifier may be used in a variety of compositions,  
including without limitation cosmetic and personal care compositions, paints,  
foods and beverages, pharmaceuticals and nutraceuticals, and home and fabric  
care compositions. Cosmetic and personal care compositions is intended to  
include, without limitation, moisturizing lotions and creams, sprays, mousses, gels  
10 including for the face and body, moisturizing cleansers and soaps, anti-aging  
products including anti-wrinkle products, anti-acne products, skin-lighteners,  
nourishing creams and lotions, firming and toning  
products, shaving creams, deodorants, color cosmetics including foundations,  
makeups, and lipsticks, suncare products such as sunscreens, suntan lotions,  
15 and after-sun products, hair conditioners and cream rinses, and shampoos, hair  
styling products including hairsprays, gels, and mousses, personal care wipes,  
baby care products, and bath and shower products.

Food and beverage compositions include without limitation sports and  
performance beverages, liquid gel products, and breads and bread products.  
20 Such products will also include food and beverage products for animals other  
than humans such as, without limitation, chickens, pigs, cattle, dogs and cats. In  
one embodiment, the emulsifier may also provide other functionality to food and  
beverage compositions such as that of improvers and softening agents for bread  
and bread products which would enhance crumb structure, softness, shelf-life  
25 and/or volume.

The compositions may include other optional components commonly used  
in the industry, and these will vary greatly depending upon the type of composition  
and the functionality and properties desired. For example, cosmetic and personal  
care applications may also include without limitation, aesthetic modifiers, UV filters,  
30 humectants, moisturizers, emollients, solvents, chelating agents, vitamins,  
antioxidants, botanical extracts, pH adjusting and neutralizing agents, preservatives,  
fragrances, active ingredients (anti-aging agents, firming or toning agents, etc.), dyes  
and pigments, conditioning agents, chelating agents, opacifiers, and foaming or anti-  
foaming agents. Other emulsifiers and/or surfactants may be added, but are not  
35 necessary for providing emulsification functionality.

In one embodiment, the compositions are substantially surfactant-free, and  
the emulsifier of the present invention is the only emulsifier present in an

5 emulsifying-effective amount. In another embodiment, no surfactant is added and no emulsifier is added to the composition other than the emulsifier of the invention.

The emulsifier emulsifies oil-in-water emulsions for use in such compositions by inclusion in the aqueous phase using techniques commonly used and known in the art. The emulsifier is substantially dissolved in the  
10 aqueous phase.

The hydrophobic phase may contain without limitation liquid or solid fatty acid triglycerides, fatty acid monoesters or diesters, silicones, long-chain alcohols, and/or vitamins. In one embodiment, the composition contains at least about 1%, in another 5 to 25%, and in a third up to 70 % of a hydrophobic phase  
15 by weight of the composition. The hydrophobic phase may be finely dispersed.

Emulsions are intended to include, without limitation, those in the form of a cream, lotion or milk or spray. As a function of the characteristics and quantity of the aqueous or hydrophobic phase, the emulsion-type compositions may contain different types of emulsions, e.g., binary oil-in-water or water-in-oil  
20 systems or multiple phase systems, such as water-in-oil-in-water or oil-in-water-in-oil systems. In another embodiment, the emulsion is in the form of a high viscosity gel.

The compositions may be adjusted to have a variety of textures, which can range from oily, to creamy to waxy. The emulsifiers provide characteristics  
25 which are desirable from the dermatological standpoint. They increase the water retention capacity of the skin and make the latter smooth and flexible. Cosmetics containing a starch derivative to be used according to the invention can be spread very well onto the skin and do not leave behind a sticky feeling.

The emulsifier may also thicken the aqueous phase of the emulsion to a desired consistency. In one embodiment, the emulsifier provides a viscosity to the  
30 aqueous phase of 400 to 30,000 cps (mPa).

The emulsifier is substantially ethoxylate-free. In one embodiment, the emulsifier contains less than 0.1% ethoxylate by weight, in another less than 0.01% ethoxylate by weight, and in still another no ethoxylate based on the weight  
35 of the emulsifier. Further, the natural base is advantageous over synthetic bases in many respects, including labeling. When used in a cosmetic composition or other composition which may come into contact with the consumer's skin, the low (or no) ethoxylate level and/or natural base reduces adverse effects on many

5 consumers, including skin irritation and sensitization, compared to many commonly used emulsifiers. For example, polyethylene glycol (PEG) is known to enable transport of pollutants to and into the skin.

The emulsifier of this invention has the further advantage of being salt tolerant. Many commonly used emulsifiers, particularly in the cosmetic and  
10 personal care industry, have poor or no salt tolerance, resulting in instability upon inclusions of salts. With the increased popularity of mineral salts, plant and sea extracts and vitamins, salt tolerance of ingredients has become more important. In one embodiment of this invention, the composition containing the emulsifier is stable with a salt content of up to 5% by weight, and in another with a salt content  
15 of up to 10% by weight. In another embodiment, the composition contains at least 1% salt by weight, and in another at least 5% salt by weight. Salt tolerance is, as is known in the art, dependent in part on the other ingredients used in the composition.

The emulsifier exhibits freeze-thaw stability and high temperature  
20 stability, making them useful in of compositions made under a variety of processing conditions. The emulsifier also has the processing advantage of not needing to be cooked (although it may be cooked) and thus may be added to a cold or hot process, with or without shear.

The emulsifier also provides a pleasant mouth- or skin-feel to the  
25 composition. This is done without significant tackiness, or grittiness, all which are viewed adversely by the consumer.

## EXAMPLES

The following examples are presented to further illustrate and explain the  
30 present invention and should not be taken as limiting in any regard. All percents used are on a weight/weight basis.

In the examples below, the following procedures/tests are used.

Funnel viscosity - To measure funnel viscosity, 38 g of the converted starch  
35 (anhydrous basis) was weighed into a tared 250 ml beaker (stainless steel) containing a thermometer and brought to 200 g total weight with distilled water. The sample was mixed to dissolve any lumps and heated or cooled to 72°F (22°C). A total of 100 ml of the cooked starch dispersion was measured into a

- 5 graduated cylinder. It was then poured into a calibrated funnel while using a finger to close the orifice. A small amount was allowed to flow into the graduate to remove any trapped air, and the complete balance remaining in the graduate was poured back into the funnel. Using a timer, the time required for the 100 ml sample to flow through the apex of the funnel was recorded.
- 10 The funnel was a standard 58 degree, thick-wall, resistance glass funnel whose top diameter was about 9-10 cm with the inside diameter of the stem being about 0.381 cm. The funnel was calibrated so as to allow 100 ml of water to go through in 6 seconds using the above procedure.
- 15 Stability testing – The cosmetic preparations described below were stability tested under the following conditions: The cosmetic preparation is stored in 125 ml glass jars for 1 months at 45 °C, 3 freeze/thaw cycles at –20 °C and 3 months at room temperature. Stability is achieved, if no significant changes in viscosity, pH, texture, color or odor are notified.
- 20 Brookfield viscosity – To measure the viscosity of cosmetic preparations described below, a Brookfield DV-I Heliopath viscometer is equipped with spindle C (the use of another spindle is notified, when appropriate). The measurement is carried out at 20 rpm at room temperature in a 125 ml glass jar.
- 25 pH measurements – pH of cosmetic preparations described below is measured with a pH-meter Orion 410A equipped with an Orion Ag/AgCl Sure-Flow Electrode at room temperature.
- 30 In the examples, the following designations and trade names are used.

Trade Name	Manufacturer	INCI Name
Neo Heliopan AV	Symrise	Ethylhexyl Methoxycinnamate
Neo Heliopan OS	Symrise	Ethylhexyl Salicylate
Parsol 1789	Roche	Butyl Methoxydibenzoylmethane
Pricerine 9091	Uniqema	Glycerin
Carbopol 1382	Noveon	Carbomer
DC 193	Dow Corning	PEG-12 Dimethicone
DC 200	Dow Corning	Dimethicone

Trade Name	Manufacturer	INCI Name
Versene 100	Dow Chemicals	Tetrasodium EDTA
Phenonip	Nipa	Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben
Triethanolamine	Merck/Rona	Triethanolamine
Sunflower Oil refined	Jan Dekker	Sunflower Oil
Lincol BAS	Eigenmann & Veronelli	C12-15 Alkylbenzoate
1,2-Propandiol	Merck/Rona	Propylene Glycol
Dry-Flo AF	National Starch & Chemical	Corn Starch Modified
Structure XL	National Starch & Chemical	Hydroxypropyl Starch Phosphate
Locron LIC	Clariant	Aluminium Chlorohydrate
Arlacel 1690	Uniqema	Sorbitan Isostearate & Polyglyceryl-3 Ricinoleate
Germaben IIE	International Specialty Polymers	Propylene Glycol & Diazolidinylurea & Methylparaben & Propylparaben
Arlamol E	Uniqema	PPG-15 Stearyl Ether
Atlas G-2330	Uniqema	Sorbeth-30
Euxyl K400	Schülke & Mayer	Phenoxyethanol & Methylidibromo Glyutaronitril
Estol 3603	Uniqema	Caprylic/Capric Triglyceride
Estol 1514	Uniqema	Isopropyl Myristate
Hansanol 1214	Hansa Chemie	C12-C14 Fatty Alcohol
Drakeol 10 LT	Penreco	Mineral Oil
Estol 1517	Uniqema	Isopropyl Palmitate
Pionier 7028	Hansen & Rosenthal	Mineral Oil
Sodium Chloride p.A.	Fluka	Sodium Chloride
Calcium Chloride p.A.	Fluka	Calcium Chloride
Crodacol C95	Croda	Cetyl Alcohol
Pristerene 4911	Uniqema	Stearic Acid
Crodacol CS90	Croda	Cetearyl Alcohol
Veegum Ultra	Vanderbilt Corp.	Magnesium Aluminium Silicate
Keltrol CG RD	Kelco	Xanthan Gum

#### Example 1 – Preparation of Component 1

##### a) Crosslinked Hydroxypropylated and Crosslinked Acetylated Waxy Corn

- 10 A total of 1000 parts waxy corn starch was introduced into a reaction vessel containing a solution of 18.75 parts sodium hydroxide and 250 parts sodium sulfate in 1500 parts water. 84 grams (8.4% on the weight of starch) of propylene oxide was added and the vessel was sealed. The contents were allowed to react for 16 hours at 40°C while the vessel was continuously tumbled to assure uniform

5 suspension of the starch throughout the reaction time. After 16 hours, the vessel was removed from the tumbler, placed in a continuously agitated container and allowed to cool to 30°C.

At that point, 0.175 gram (0.0175% on starch weight or 0.106 mL) of phosphorous oxychloride was added and allowed to react for 30 minutes. The pH  
10 of the resultant suspension was then adjusted to 3.0-3.4 by the addition of a 25% sulfuric acid solution and held for 1 hour. The pH was finally adjusted to 5.5 with 3% sodium hydroxide, and the hydroxypropylated/crosslinked starch was recovered by filtration, washed two times with 1500 parts water. The starch was then cooked and dried using the methods of US 4,280,851 and US 4,600,472.

15 b) STMP Crosslinking

A total of 1000 parts waxy corn starch was introduced into a reaction vessel containing a solution of 18.75 parts sodium hydroxide, 250 parts sodium sulfate and the desired amount of STMP in 1500 parts water. The required amount of propylene oxide was added and the vessel was sealed. The contents were  
20 allowed to react for 16 hours at 40°C while the vessel was continuously tumbled to assure uniform suspension of the starch throughout the reaction time. After 16 hours, the vessel was removed from the tumbler, placed in a continuously agitated container and allowed to cool to 30°C.

The pH of the resultant suspension was then adjusted to 3.0-3.4 by the addition  
25 of a 25% sulfuric acid solution and held for 1 hour. The pH was finally adjusted to 5.5 with 3% sodium hydroxide, and the hydroxypropylated/crosslinked starch was recovered by filtration, washed two times with 1500 parts water. The starch was then cooked and spray dried.

c) Adipic-Acetic Crosslinking

30 The adipic-acetic crosslinking reagent was prepared by adding 20 gm adipic acid to 180 gram acetic anhydride on a 500 ml Erlenmeyer flask placed in a water bath. While agitating the mixture, the water bath is heated to 90°C gradually over 1 hour and held at 90°C for an additional hour. The mixture is then cooled to room temperature and stored in a glass jar.

35 A total of 1000 parts waxy corn starch was introduced into a reaction vessel containing a solution of 18.75 parts sodium hydroxide and 250 parts sodium sulfate in 1500 parts water. The required amount of propylene oxide was added and the vessel was sealed. The contents were allowed to react for 16 hours at

5     40°C while the vessel was continuously tumbled to assure uniform suspension of the starch throughout the reaction time. After 16 hours, the vessel was removed from the tumbler, placed in a continuously agitated container and allowed to cool to 30°C.

10     The pH was adjusted to 8.0 (using 25% sulfuric acid) and the desired amount of adipic-acetic reagent was added while the pH was controlled to a range of 7.8 and 8.2 with a 3% sodium hydroxide solution. Once all of the adipic-acetic reagent was added and the pH stabilized, the pH was then adjusted to 3.0-3.4 by the addition of a 25% sulfuric acid solution and held for 1 hour. The pH was finally adjusted to 5.5 with 3% sodium hydroxide, and the hydroxypropylated /  
15     crosslinked starch was recovered by filtration, washed two times with 1500 parts water, cooked, and dried.

d)     Acetic anhydride with adipic-acetic crosslinking

A total of 1000 parts waxy corn starch was introduced into a reaction vessel containing 1500 parts water at 25°C. The pH was adjusted to 8.0 (using 3%  
20     sodium hydroxide) and the desired amount of both acetic anhydride and adipic-acetic reagent (prepared as above) was slowly added while the pH was controlled to a range of 7.8 and 8.2 with a 3% sodium hydroxide solution. Once all of the acetic anhydride and adipic-acetic reagent were added and the pH stabilized, the pH was then adjusted to 5.5 with dilute hydrochloric acid, and the acetylated /  
25     crosslinked starch was recovered by filtration, washed two times with 1500 parts water, cooked and dried.

e)     Example 1a was repeated using tapioca starch in place of the corn starch.

### 30     Example 2 – Preparation of Component 2

(a)     An octenylsuccinate derivative (OSA) of waxy maize starch was prepared by the method disclosed in Example II of U.S. Pat. No. 2,661,349 except that the corn starch was replaced by waxy maize. In addition, the starch was reacted with 3% octenylsuccinic acid anhydride, rather than with 0.5% as disclosed in the  
35     reference. A 28% aqueous slurry of the OSA waxy maize was jet cooked at approximately 300°F (149°C). Thereafter, the cooked OSA waxy maize was placed in a constant temperature bath and maintained at 55°C with constant stirring. The pH was adjusted to 5.3 with 3% hydrochloric acid.



5           The cooked OSA waxy maize dispersion was divided into four batches  
and a different level of barley beta-amylase (1,4-alpha-D-glucan maltohydrolase  
(E.C. 3.2.1.2), obtained from Fermco Biochemics, Inc., Elk Grove Village, Ill.) was  
added to each batch. The amounts of enzyme added were 168, 334, 840 and  
10       1,110 DP.degree. per 100 g dry basis of OSA waxy maize for approximately eight  
hours.

          The degree of degradation was determined by monitoring the funnel  
viscosity of the dispersion. Accordingly, the level of alpha-amylase contamination  
present in the barley beta-amylase was monitored and limited to no more than 0.4  
DU/ml of enzyme solution so that the viscosity would not be affected by this  
15       variable. A DU (Dextrinizing Unit) is the quantity of alpha-amylase that will  
dextrinize soluble starch, in the presence of an excess of beta-amylase, at the  
rate of 1 gm/hour at 20°C.

          By carefully controlling the parameters of the funnel viscosity test and  
limiting alpha-amylase contamination, the degree of starch degradation by beta-  
20       amylase was correlated to the loss in viscosity. The reducing sugars were  
measured by the Fehling method to confirm the degree of degradation.

          In this example, the desired enzyme reaction end point was reached  
within a funnel viscosity range from 9-50 seconds. The reducing sugars content  
of these samples ranged from 29-35%. The corresponding degradation of the  
25       starch, by weight, ranged from 58-70%. When the targeted viscosity was  
reached, the enzyme was deactivated by injection of live steam into the reaction  
solution until a temperature of at least 75°C was attained and held for at least 15  
min. The batches were then spray-dried at an inlet temperature of 200-210°C and  
an outlet temperature of 85-90°C using a standard #22 11/4 J nozzle obtained  
30       from Spraying Systems Company. The spray-dried starch product was screened  
through #40 mesh screen.

(b)       The beta-amylase degraded OSA waxy maize prepared by the method  
set forth in Example 2(a) was subjected to dialysis to remove maltose. The starch  
was dispersed in distilled water at 15-20% solids and placed in a dialysis tube  
35       (obtained from Spectropor Membrane) that retained molecules with molecular  
weights in excess of 6,000-8,000. The dispersion was dialyzed against distilled  
water until the dialyzate was free of all organic materials. The starch was then  
collected by precipitation with ethanol.

5 (c) Example 2(a) was repeated except that dodecenylsuccinic acid anhydride was substituted for octenylsuccinic acid anhydride

(d) Example 2(a) was repeated with a reversed the sequence of steps. A 28% solids aqueous slurry of waxy maize starch was prepared, the pH was adjusted to 6.0-6.3 by the addition of 3% NaOH, and the slurry was jet-cooked at  
10 approximately 300°F (149°C). The cooked starch was placed in a constant temperature water bath and maintained at 55-60°C with constant stirring. The barley beta-amylase used in Example 2(a) was added to the cooked starch at a concentration of 1,650 DP degree per 100 g dry basis of starch. The batch of beta-amylase used in this example contained 0.9 DU/ml of alpha-amylase  
15 activity. The degree of degradation was monitored by the funnel viscosity procedure.

When the starch had reached a funnel viscosity of 30 seconds, the enzyme was deactivated by adding 10% HCl to lower the pH to 3.5-4.0, and holding the starch at this pH for 30-60 minutes. After deactivation, the pH was  
20 adjusted to 7.0 by adding 3% NaOH.

The OSA derivative was prepared by thoroughly blending 3 g of octenylsuccinic acid anhydride per 100 g dry weight basis of starch into the neutralized, debranched starch dispersion. The reaction was permitted to continue at room temperature with good agitation for 4 hours.

25 A portion of this starch dispersion was spray-dried by the method set forth in Example 2(a).

(e) 500 grams of waxy maize starch were slurried in 750 ml water. The pH was adjusted to 7.5 using 3% sodium hydroxide. 15 grams of octenylsuccinic anhydride (OSA) were added in one-third increments every thirty minutes while  
30 maintaining the pH at 7.5 using 3% sodium hydroxide and constant agitation. The starch was then filtered out and washed with 750 ml water. The starch was then reslurried in 500 ml water and the pH adjusted to 5.5 with 3:1 hydrochloric acid. The starch was then filtered, washed with 750 ml water, and air dried to produce an OSA starch.

35 600 grams of such OSA derivatized starch were mixed with 400 grams glucose.

(f) A cold water soluble, mildly acid degraded OSA starch was prepared by using the derivatized starch of Example 2(e), hydrolyzing using acid to a fluidity of

- 5 about 60, and spray drying the starch. 600 grams of this starch were mixed with 400 grams glucose.
- (g) 500 grams of the starch prepared as in Example 2(f) were mixed with 500 grams maltose.
- (h) 340 grams of an OSA derivatized starch prepared as in Example 2(e)
- 10 were mixed with 660 grams maltose.
- (i) 550 grams of an OSA derivatized starch prepared as in Example 2(e) were mixed with 450 grams glucose.
- (j) 500 grams of an OSA derivatized starch prepared as in Example 2(e) were mixed with 500 grams glucose.
- 15 (k) 400 grams of an OSA derivatized starch prepared as in Example 2(e) were mixed with 600 grams glucose.

Example 3 -

The following samples of the emulsifier of this invention have been made.

<u>Sample</u>	<u>Component 1</u>	<u>Component 2</u>
Sample 1	50% starch of example 1a	50% starch of example 2a
Sample 2	67% starch of example 1a	33% starch of example 2a
Sample 3	80 % starch of example 1a	20% starch of example 2a
Sample 4	50% starch of example 1a	50% starch of example 2f
Sample 5	67% starch of example 1a	33% starch of example 2f
Sample 6	80 % starch of example 1a	20% starch of example 2f

## 5 Example 4

The following creams have been prepared with the emulsifier describe in example 3 as sample 1, sample 2 resp. sample 3.

INCI-Designation	4a	4b	4c	4d	4e	4f	4g	4h	4i	4j	4k	4l
Sunflower Oil	10.0	-	40.0	-	10.0	-	40.0	-	10.0	-	40.0	-
C12-15 Alkylbenzoate	-	10.0	-	40.0	-	10.0	-	40.0	-	10.0	-	40.0
Sample 1	5.0	5.0	5.0	5.0	-	-	-	-	-	-	-	-
Sample 2	-	-	-	-	5.0	5.0	5.0	5.0	-	-	-	-
Sample 3	-	-	-	-	-	-	-	-	5.0	5.0	5.0	5.0
Phenoxyethanol &Methylparaben &Ethylparaben& Propylparaben	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
D.I. Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Sum W/W%	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Viscosity [mPas]	550	600	15550	na**	1500	1200	15500	20800	1900	2050	11700	18550
pH	4.4	4.4	4.4	na	4.5	4.8	4.6	5.6	5.0	5.2	4.9	5.1

\*W/W% \*\* no emulsification achieved

10 The following creams have been prepared with the emulsifier describe in example 3 as sample 4, sample 5 resp. sample 6.

INCI-Designation	4m	4n	4o	4p	4q	4r	4s	4t	4u	4v	4w	4x
Sunflower Oil	10.0	-	40.0	-	10.0	-	40.0	-	10.0	-	40.0	-
C12-15 Alkylbenzoate	-	10.0	-	40.0	-	10.0	-	40.0	-	10.0	-	40.0
Sample 4	5.0	5.0	5.0	5.0	-	-	-	-	-	-	-	-
Sample 5	-	-	-	-	5.0	5.0	5.0	5.0	-	-	-	-
Sample 6	-	-	-	-	-	-	-	-	5.0	5.0	5.0	5.0
Phenoxyethanol &Methylparaben &Ethylparaben& Propylparaben	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
D.I. Water	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Sum W/W%	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Viscosity [mPas]	800	850	13900	na**	1700	1300	na	na	2700	2850	na	na
pH	4.2	4.2	4.4	na	4.5	4.5	na	na	4.7	4.7	na	na

\*W/W% \*\* no emulsification achieved

5

Preparation: The emulsifier was dispersed in deionized (D.I.) water and stirred until hydration was fully achieved. The preservative and oil were added while stirring using an overhead mixer at 900 rpm. The mixture was homogenized for one minute at 13,000 rpm.

10

#### Example 5

##### **a) O/W Lotion 11815-32**

<b>INCI Designation</b>	<b>W/W%</b>
Mineral Oil	10.0
Sample 2	5.0
Isopropyl Palmitate	5.0
Glycerin	3.0
Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben	1.0
D.I. Water	ad 100.0

Preparation: The emulsifier was dispersed in a mixture of D.I. water and glycerin and stirred until the starch was fully hydrated. The other components were premixed and added to the water phase while stirring at 900 rpm. The mixture was then homogenized for two minutes at 10,000 rpm.

Viscosity 5,000 mPas

pH 5.0

##### **20 b) O/W Milk 11814-65B**

<b>INCI Designation</b>	<b>W/W%</b>
Mineral Oil	8.0
Sample 2	4.0
PPG-15 Stearyl Ether	3.5
Propylen Glycol & Diazolidinylurea & Methylparaben & Propylparaben	0.25
D.I. Water	ad 100.0

Preparation: The emulsifier was dispersed in D.I. water and stirred until the starch was fully hydrated while heating to 80°C. The oil components were premixed,

- 5 heated to 80°C and added to the water phase while stirring at 900 rpm. Stirring continued while cooling, and the preservative were added at 30°C.

Viscosity 2,000 mPas

pH 5.3

10 c) Daily UV Cream 11815-42

INCI Designation	W/W%
Sample 2	5.0
Corn Starch Modified	4.0
Propylene Glycol	4.0
Ethylhexyl Salicylate	3.5
Ethylhexyl Methoxycinnamate	3.1
Glycerin	2.0
Hydroxypropyl Starch Phosphate	1.0
Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben	1.0
Tetrasodium EDTA	0.2
Carbomer	0.15
D.I. Water	ad 100.0
Triethanolamine	ad pH 6.5

- Preparation: Carbopol, the emulsifier and Hydroxypropyl Starch Phosphate were dispersed in D.I. water and stirred until all ingredients were fully hydrated. Tetrasodium EDTA and glycerin were added and heated to 80°C. The other
- 15 Tetrasodium EDTA and glycerin and heat to 80°C. Premix the other components with exception of Triethanolamine, Corn Starch Modified and Propylene Glycol were premixed, heated to 80°C and added to the water phase while stirring at 900 rpm. Stirring continued while cooling to 45°C. Corn Starch Modified was dispersed in Propylene Glycol and added to the emulsion. The mixture was
- 20 homogenized for two minutes at 10,000 rpm and pH was adjusted with Triethanolamine.

Viscosity 19,500 mPas

pH 6.5

5 d) **AP/Deo Lotion 11814-65A**

INCI Designation	W/W%
Sample 2	4.0
Aluminium Chlorohydrate (50 % Soln.)	40.0
Sorbitan Isostearate & Polyglyceryl-3 Ricinoleate	1.0
PPG-15 Stearyl Ether	4.0
Sorbeth-30	1.5
Propylen Glycol & Diazolidinylurea & Methylparaben & Propylparaben	0.25
D.I. Water	ad 100.0

Preparation: The emulsifier was dispersed in D.I. water and stirred until the starch was fully hydrated while heating to 75°C. The oil components were premixed, heated to 75°C and added to the water phase under homogenization for at least 5 minutes. Stirring continued while cooling; and the preservative was added at 30°C.

Viscosity 2,050 mPas

pH 4.4

15 Example 6

The following emulsions demonstrate the extraordinary salt tolerance of the emulsifier:

INCI-Designation	6a	6b	6c	6d
C12-15 Alkylbenzoate	10.0	10.0	10.0	10.0
Sample 2	5.0	5.0	5.0	5.0
Phenoxyethanol & Methylparaben & Ethylparaben & Propylparaben	1.0	1.0	1.0	1.0
Sodium Chloride	2.0	10.0	-	-
Calcium Chloride	-	-	2.0	10.0
D.I. Water	ad 100.0	ad 100.0	ad 100.0	ad 100.0

20 Preparation: The emulsifier was dispersed in D.I. water and stirred until hydration was fully achieved. The preservative, oil and salt were added while stirring at 900 rpm.

## 5 Example 7

The following emulsions demonstrate the broad compatibility with different oils as well as the excellent emulsifying properties being independent of HLB required by the oil phase:

INCI-Designation	HLB	7a	7b	7c	7d	7e	7f	7g	7h
Caprylic/Capric Triglyceride	5	10.0				-	-	-	-
PPG-15 Stearyl Ether	7	-	10.0			-	-	-	-
Sunflower Oil	8	-	-	10.0		-	-	-	-
Cyclomethicone	9	-	-	-	10.0	-	-	-	-
Mineral Oil	10	-	-	-	-	10.0	-	-	-
Isopropyl Myristate	11	-	-	-	-	-	10.0	-	-
C12-15 Alkylbenzoate	12	-	-	-	-	-	-	10.0	-
C12-C14 Fatty Alcohol	14	-	-	-	-	-	-	-	10.0
Sample 2		5.0	5.0	5.0	1.0	5.0	5.0	5.0	5.0
Phenoxyethanol & Methylidibromo Glutaronitril		0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
D.I. Water		q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.	q.s.
Sum W/W%		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

10

Preparation: The emulsifier was dispersed in D.I. water and stirred until hydration was fully achieved. The preservative and oil were added while stirring using an overhead mixer at 900 rpm and homogenized for one minute at 13,000 rpm.



## 5 Example 8

The following emulsions demonstrate the compatibility of the emulsifier with rheology modifiers and bodying systems:

INCI-Designation	8a	8b	8c	8d	8e
Cetyl Alcohol	3.0			-	-
Stearic Acid	-	3.0		-	-
Cetearyl Alcohol	-	-	3.0	-	-
Magnesium Aluminium Silicate	-	-	-	0.8	-
Xanthan Gum	-	-	-	-	0.2
Mineral Oil	10.0	10.0	10.0	10.0	10.0
Sample 2	5.0	5.0	1.0	5.0	5.0
Phenoxyethanol & Methylidibromo Glutaronitril	0.25	0.25	0.25	0.25	0.25
D.I. Water	ad 100.0	ad 100.0	ad 100.0	ad 100.0	ad 100.0

10

Preparation: The emulsifier was dispersed in D.I. water and stirred until hydration was fully achieved while heating to 75°C. The oils and rheology modifier were mixed together and heated to 75°C. The oil phase was added to the water phase while stirring. The preservative was added when the mixture was cooled to 40°C

15 and then homogenized for one minute at 13,000 rpm.